

## **Thermophysical Properties of Simple Liquid Metals: A Brief Review of Theory**

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In this paper, we review the current theory of the thermophysical properties of simple liquid metals. The emphasis is on thermodynamic properties, but we also briefly discuss the nonequilibrium properties of liquid metals. We begin by defining a "simple liquid metal" as one in which the valence electrons interact only weakly with the ionic cores, so that the interaction can be treated by perturbation theory. We then write down the equilibrium Hamiltonian of a liquid metal as a sum of five terms: the bare ion-ion interaction, the electron-electron interaction, the bare electron-ion interaction, and the kinetic energies of electrons and ions. Since the electron-ion interaction can be treated by perturbation, the electronic part contributes in two ways to the Helmholtz free energy: it gives a density-dependent term which is independent of the arrangement of ions, and it acts to screen the ion-ion interaction, giving rise to effective ion-ion pair potentials which are density-dependent, in general. After sketching the form of a typical pair potential, we briefly enumerate some methods for calculating the ionic distribution function and hence the Helmholtz free energy of the liquid: monte Carlo simulations, molecular dynamics simulations, and thermodynamic perturbation theory.

The final result is a general expression for the Helmholtz free energy of the liquid metal. It can be used to calculate a wide range of thermodynamic properties of simple metal liquids, which we enumerate. They include not only a range of thermodynamic coefficients of both metals and alloys, but also many aspects of the phase diagram, including freezing curves of pure elements and phase diagrams of liquid alloys (including liquidus and solidus curves). We briefly mention some key discoveries resulting from previous applications of this method, and point out that the same methods work for other materials not normally considered to be liquid metals (such as colloidal suspensions, in which the suspended microspheres behave like ions screened by the salt solution in which they are suspended).

We conclude with a brief discussion of some non-equilibrium (i.e., transport) properties which can be treated by an extension of these methods. These include electrical resistivity, thermal conductivity, viscosity, atomic self-diffusion coefficients, concentration diffusion coefficients in alloys, surface tension and thermal emissivity. Finally, we briefly mention two methods by which the theory might be extended to non-simple liquid metals: these are empirical techniques (i.e., empirical two- and three-body potentials), and

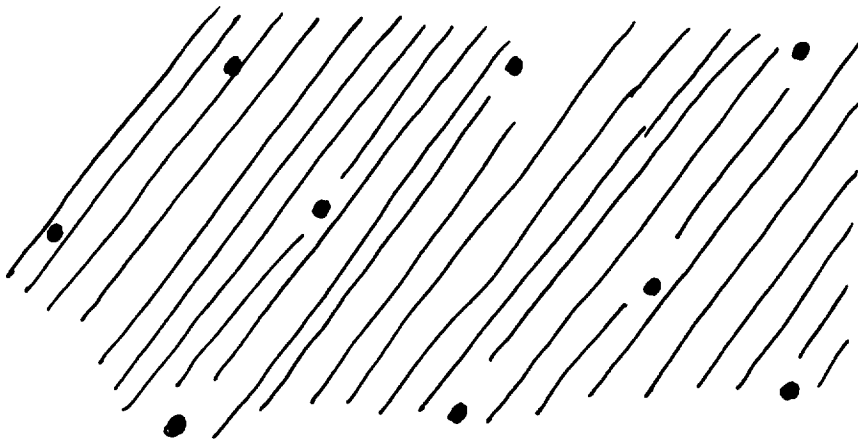
numerical many-body approaches. Both may be potentially applicable to extremely complex systems, such as nonstoichiometric liquid semiconductor alloys.

### **What is a “Simple Liquid Metal”?**

A simple liquid metal is one in which electrons can be unambiguously divided into two categories - “valence” electrons and “core” electrons - such that the interaction between the valence electrons and the ionic core is sufficiently weak to be treated by low-order perturbation theory. Examples: alkali metals, alkaline earths, several polyvalent metals (such as Al, In). The transition and noble metals are not simple metals.

## **“Plum Pudding” Model of a Liquid Metal**

- Heavy dots: ions of charge  $Z|e|$
- Cross-hatching: electron gas (valence electrons, charge  $-|e|$ )



Hamiltonian of a simple liquid metal is

$$H = \frac{1}{2} \sum_{\mathbf{R} \neq \mathbf{R}'} \frac{Z^2 e^2}{|\mathbf{R} - \mathbf{R}'|} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{\mathbf{r}_i, \mathbf{R}} V_{ps}(|\mathbf{r}_i - \mathbf{R}|) \\ + \sum_i \frac{p_i^2}{2m} + \sum_{\mathbf{R}} \frac{P_{\mathbf{R}}^2}{2M}$$

- $\mathbf{R}$  = ionic position (ions of valence  $Z$ )
- $\mathbf{P}_{\mathbf{R}}$  = ionic momentum
- $\mathbf{r}_i$  = electronic position
- $\mathbf{p}_i$  = electronic momentum
- $V_{ps}$  = electron-ion interaction (“pseudopotential”)

$F$  = Helmholtz free energy =  $k_B T \ln Z$

$$Z = \frac{1}{h^{3N}} \int \Pi_{\mathbf{R}} d\mathbf{R} d\mathbf{P}_{\mathbf{R}} \text{Tr}_e \exp\left(-\frac{H}{k_B T}\right)$$

Here  $h$  = Planck’s constant, “ $\text{Tr}_e$ ” denotes a trace over electronic coordinates. The ions are taken to be classical particles, while the valence electrons are assumed quantum-mechanical.

Rewrite partition function  $Z$  as:

$$Z = \frac{1}{h^{3N}} \int \Pi_{\mathbf{R}} d\mathbf{R} d\mathbf{P}_{\mathbf{R}} e^{-\beta H_{ii}} [Tr_e e^{-\beta(H_{ee} + H_{ei})}]$$

- $H_{ii}$  = first and fifth terms in Hamiltonian on previous page
- $H_{ee}$  = second and fourth terms
- $H_{ei}$  = third term
- $\beta = 1/k_B T$ .

We can now rewrite the electronic trace as

$$Tr_e[\dots] = \exp(-\beta F'_e(\{\mathbf{R}\})),$$

where  $F'_e$  is the free energy of an electron gas in the “external potential” produced by  $N$  ions located at  $(\mathbf{R}_1, \dots, \mathbf{R}_N)$ .

In turn,

$$F'_e = F_{eg} + E_{BS}$$

- $F_{eg}$  = free energy of a uniform interacting electron gas in a uniform positive background.
- $E_{BS}$  = “band-structure energy” = extra piece in free energy due to electron-ion interaction. In spite of its name, the band-structure energy does not imply a periodic lattice.

If  $V_{ps}$  is weak, we can do perturbation theory to estimate  $E_{BS}$ . Band-structure energy in weak-pseudopotential limit is

$$E_{BS} \approx \frac{1}{2} \sum_{\mathbf{q} \neq 0} \chi_e(\mathbf{q}) |V_{ps}(\mathbf{q}) \rho(\mathbf{q})|^2$$

$$\chi_e(\mathbf{q}) = \frac{q^2}{4\pi e^2} \left( \frac{1}{\epsilon(q)} - 1 \right)$$

$$\rho(\mathbf{q}) = \sum_{\mathbf{R}} e^{-i\mathbf{q} \cdot \mathbf{R}},$$

where  $\epsilon(q)$  = dielectric function of interacting electron gas. ( $q = 0$  term is not small and treated separately.)

We can now express the partition function in terms of ionic coordinates alone:

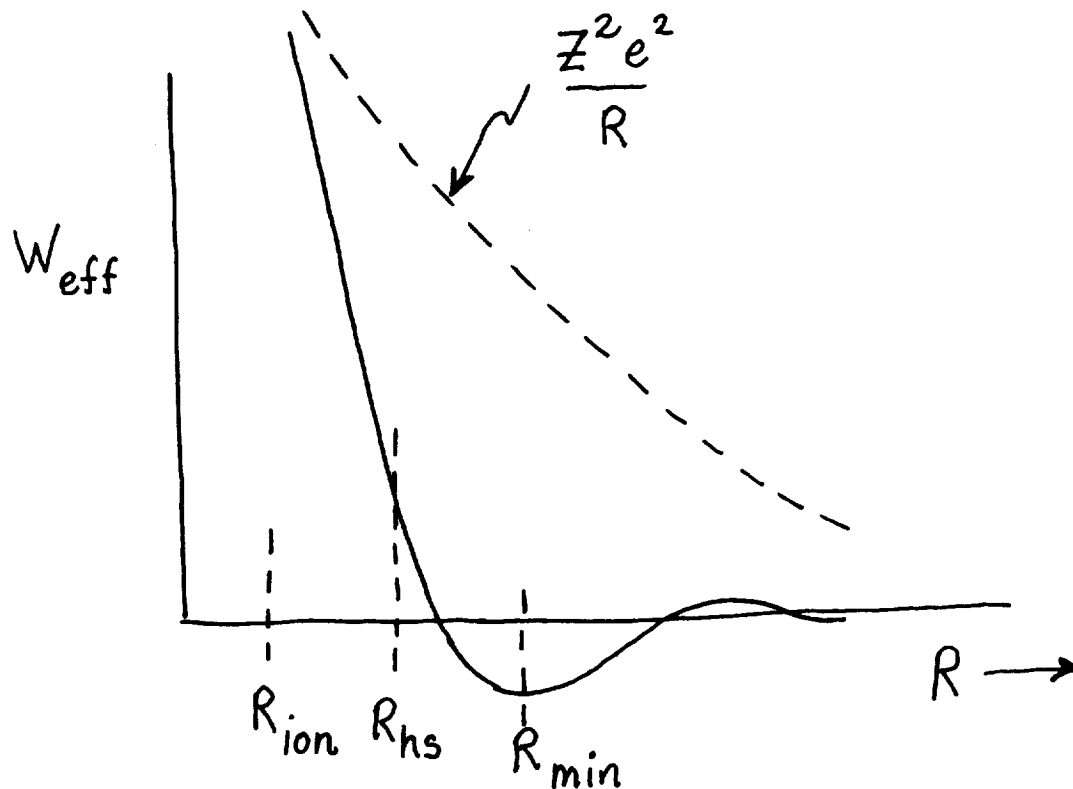
$$Z = \frac{1}{h^{3N}} \int \Pi_{\mathbf{R}} d\mathbf{R} d\mathbf{P}_{\mathbf{R}} \exp\{-\beta[W_{eff}(\{\mathbf{R}\}, n_e) + \sum_{\mathbf{R}} \frac{\mathbf{P}_{\mathbf{R}}^2}{2M}]\},$$

where  $W_{eff}$  is an effective potential energy, which has the form

$$W_{eff}(\{\mathbf{R}, n_e\}) = \frac{1}{2} \sum_{\mathbf{R} \neq \mathbf{R}'} \frac{Z^2 e^2}{|\mathbf{R} - \mathbf{R}'|} + E_{BS}(\{\mathbf{R}\}) + F_{eg}(n_e).$$

Note that  $E_{BS}$  is a density-dependent, structure-independent part, plus a sum of two-body contributions (if  $V_{ps}$  is weak). This leads to effective pairwise interionic interactions.

## Schematic of a Typical Pair Potential



- $R_{\text{min}} \approx$  nearest-neighbor separation
- $R_{\text{hs}} \approx$  effective (temperature-dependent) hard-sphere diameter  $\approx$  distance of closest approach at temperature  $T$ .
- $R_{\text{ion}} =$  ionic diameter ( $R_{\text{ion}} < R_{\text{hs}}$ ).



Given the pair potential, the ionic distribution function can be calculated by several methods. For example:

- Monte Carlo simulation: a statistical sampling of configuration space, with weight proportional to the Boltzmann factor;
- Molecular dynamics: solve Newton's equation of motion numerically at a given energy  $E$  (or temperature  $T$ );
- Thermodynamic perturbation theory (approximate the liquid structure factor by that of a known liquid system (e. g., a liquid of hard spheres), then obtain "best" parameters (e. g., the hard-sphere diameter) variationally. This procedure gives a temperature and density-dependent effective hard-sphere diameter.

## Results

$$F = E_M + E_{BS} + E_0 - TS_{ion} + F_{eg} + \frac{3}{2}Nk_B T$$

- $E_M$  = Madelung energy (bare ion-ion interaction energy)
- $E_{BS}$  = band-structure energy
- $E_0$  = "Hartree" energy (sum of long-wavelength terms in potential energy)
- $S_{ion}$  = ionic entropy
- $F_{eg}$  = free energy of uniform, interacting electron gas.

## Some Calculable Quantities

- Free energy  $F = E - TS$
- Internal energy  $E$
- Entropy  $S$
- Specific Heat  $C_V$
- Thermal expansion coefficient  $\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P$
- Isothermal compressibility  $\kappa_T = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T$
- Liquid structure factor  $S(q)$
- Equation of state  $P(V, T)$
- Heat of formation (of elements)
- Heat of mixing (of alloys)
- Freezing curve (of pure elements) (i. e. line in P-T plane on which the liquid element freezes)
- Properties on the freezing curve ( $\Delta S, \Delta V$ )
- Phase diagrams of liquid alloys (phase separation curves in concentration-temperature plane, liquidus, solidus, eutectic points)

## Some Comments on Specific Properties

- $C_V$  generally dominated by ions. (Valence electrons are in their ground state, or nearly so, at least for simple liquid metals.)
- $\kappa_T$  dominated by electrons. (Here, the density-dependent, structure-independent part of the free energy is crucial.)
- Melting temperatures of pure elements reduced by screening ( $E_{BS}$ ). ( $E_{BS}=0$  corresponds to the well-known “one-component plasma”.) The reduction is about 30% for the alkali metals, more than 80% for most polyvalents (Al, In, etc.).
- Same theory for freezing also works for “colloidal crystals” (suspensions of charged polystyrene microspheres in a salt solution (Shih and Stroud, 1983).

## Non-equilibrium (transport) properties of simple liquid metals

- **DC electrical resistivity.** Reasonable agreement with weak-scattering (Ziman) formula

$$\rho \propto \int_0^{2k_F} k^3 |V_{ps}^{scr}(k)|^2 S(k) dk$$

where  $S(k)$  is the structure factor and  $V_{ps}^{scr}(k)$  is the screened electron-ion pseudopotential.

- **Thermal conductivity.** There are two contributions: (i) electronic; (ii) ionic. Electronic contribution dominates in simple liquid metals, and can be calculated from  $\rho$  using Wiedemann-Franz law (this is not true in poorly-conducting liquid semiconductors).
- **Viscosity, Atomic Self-Diffusion Coefficient, Concentration Diffusion Coefficients in Alloys.** All these quantities are dominated by the screened pair potentials described above, and can be calculated from them by molecular dynamics simulations, or estimated from hard-sphere results (using variationally determined hard-sphere diameters).

## Other Properties.

- **Surface Tension  $\gamma$ .** Reasonable results can be obtained from an “ionic density functional theory” which considers the free energy of an inhomogeneous liquid in terms of the free energy and response functions of a homogeneous liquid (Wood and Stroud, 1983; Zeng and Stroud, 1986). Good results also for surface entropy  $-\frac{d\gamma}{dT}$ .
- **Thermal Emissivity.** This requires knowledge of reflectivity  $R(\omega)$  (or equivalently, complex dielectric function  $\epsilon(\omega)$ ) as a function of frequency in the infrared. The Drude model is probably inadequate, even for simple metals; one should include band-structure effects at least in perturbation theory.

## **Extension to Non-Simple Metals (or to Liquid Semiconductors)**

There are several possibilities:

- Use empirical (two-body and three-body) potential fitted to appropriate experiments. This is not very well justified from first principles, but may work in selected noble and transition metals, or liquid semiconductors.
- Use numerical many-body techniques. This technique was pioneered by Car and Parrinello. It is very computer-intensive, but may be the best method for extremely complex systems, such as nonstoichiometric liquid semiconductor alloys. With the advent of large computers, it may become feasible in the near future, both for thermodynamic and for transport properties.

## **Conclusion**

Theory is rapidly improving!